

# AN APPROACH TO PROCESSABLE PMR POLYIMIDES

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## Introduction

The use of polymer matrix composites (PMC's) in aircraft engines can lead to substantial weight savings over metals. This weight reduction correlates into better fuel economy, increased speed, and increased passenger load.<sup>1</sup> Typically, high performance PMC's possess high thermal-oxidative stabilities (TOS) and high glass transition temperatures ( $T_g$ 's) to withstand temperatures up to 316°C (600°F).

One of the leading high temperature resins systems available today is PMR-15<sup>2</sup> (Polymerization of Monomeric Reactants, MW=1500).<sup>3</sup> This thermosetting polyimide utilizes addition curing through polymer endcaps, which enables hand lay-up processing of carbon fiber composite parts with low void contents. However, the large amount of hand labor raises manufacturing costs and prohibits the use of PMR-15 in many aerospace applications. Resin Transfer Molding (RTM) provides an economical alternative, but it requires a melt viscosity of <10<sup>3</sup> centipoise (cP). This is much lower than the minimum melt viscosity of PMR-15 (about 10<sup>4</sup> cP). To improve the processability of polyimides, the polymer backbone can be modified by incorporating flexible linkages, such as branching, bulky pendant groups, kinked structures, and twisted or non-coplanar moieties.<sup>4-6</sup> The focus of this paper will be the introduction of non-coplanar biaryls into the PMR polyimide backbone to increase processability while maintaining high temperature performance.

## Experimental

**Materials.** 2,2'-Bis(3,4-dicarboxyphenoxy)1,1'-biphenyl dianhydride (PBDA) was prepared as described by Liou, et al.<sup>10</sup> 2,2'-Bis(4-aminophenoxy)1,1'-biphenyl (BPAP) was synthesized by Dr. Dan Hubbard at Grambling State, Grambling, LA. Bisaniline xylene (BAX) was synthesized by Dr. David Klopotek at St. Norbert College, DePere, WI. Methylene dianiline (MDA) was purchased from Dexter Corporation. BAPP and DMBz (Figure 1) were purchased from Wakayama Seika Kogyo Company, and BTDA, NE, and *p*-PDA (Figure 1) were purchased from Chriskev Company. Dimethyl ester/acids (BTDE and PBDE) were prepared by placing BTDA and PBDA under reflux in methanol for 2 and 6 hours, respectively.

**Instrumentation.** Glass transition temperatures ( $T_g$ 's) were measured on a TA Model 2940 Thermomechanical Analyzer (TMA) with expansion probe (heating rate of 10°C/min., air purge). Infrared spectra were obtained on a Nicolet Model 510P Fourier Transform Infrared Spectrometer (FTIR), and thermogravimetric analyses (TGA) were performed on a TA Model 2950 TGA (heating rate of 10°C/min., with air and N<sub>2</sub> purges).

**Molding Powder Preparation.** In a glass jar, diamine ( $n+1$  equivalents) was added to a 50-weight % solution of PBDE in methanol ( $n$  equivalents) and was stirred until completely dissolved. Then, the endcap (NE) was added, and the solution was heated and magnetically stirred on a hot plate until most of the methanol evaporated. At this time, the stir bar was removed, and the resulting resin was heated (or B-staged) in an air circulating oven for 2 hr. at 204°C, 0.5 hr. at 260°C, and an additional 0.5 hr. at 288°C. After cooling to room temperature, the rigid resin was scraped out of the jar and was ground into a fine powder. FTIR and TGA confirmed complete imidization.

**Neat Resin Processing.** The molding powder (1.25 g) was placed in a 2.54 cm diameter matched steel mold and heated to 316°C with contact pressure. Pressure was applied (about 17 MPa), and the mold remained there for 1.5 hr. The resulting disks were postcured by ramping to a final temperature of 329°C and holding there for 12 hr.

**Isothermal Aging.** Pieces of the postcured neat resin disk (about 1cm<sup>2</sup>) were aged for 1000 hrs. at 288°C in an air-circulating oven (100 cm<sup>3</sup>/min. airflow). Samples were withdrawn after 100, 250, 500, 750, and 1000 hr., placed in a desiccator while cooling to room temperature, and weighed on an analytical balance (+/- 0.0001 g).

## Results and Discussion

**Neat Resins with  $n=2$ .** The oligomer structure with  $n=2$  (calc.) is

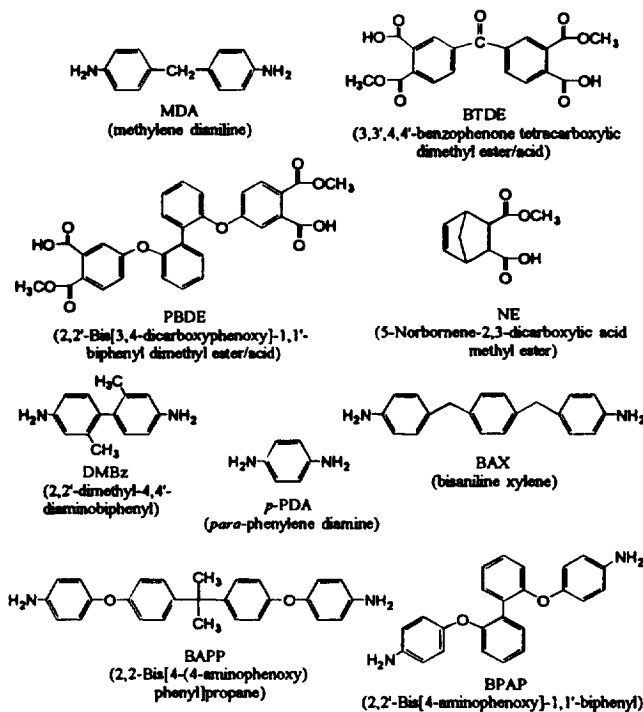


Figure 1. Monomeric reactants used in this study.

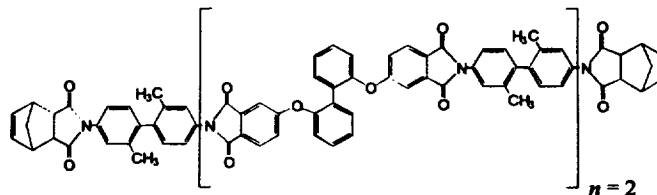


Figure 2. Example of PMR oligomeric structure with DMBz and PBDA.

shown in Figure 2. All formulations were prepared according to the scheme PBDE/DIAMINE/NE,  $n=2$ , and the controls, PMR-15 and AMB-21, were prepared according to the schemes BTDE/MDA/NE,  $n=2$  and BTDE/BAPP/NE,  $n=2$ , respectively.

Glass transition temperatures of the postcured resin disks are displayed in Figure 3. The  $T_g$ 's shown represent the average of three separate batches of the same formulation, and the error bars portray the standard deviation between the three batches. The highest  $T_g$ 's were obtained from the most rigid diamines, namely *p*-PDA and DMBz. As the flexibility of the diamine increases, the  $T_g$  of the polyimide decreases. All of the  $T_g$ 's are lower than PMR-15, but the DMBz formulation is comparable to AMB-21. Interestingly, Liou and coworkers have reported<sup>9,10</sup> that the  $T_g$  of aromatic polyimides will increase by 50°C or more when the biphenyl moiety is substituted with a binaphthyl moiety. It is also believed that processability will increase by the introduction of 2,2' substituted binaphthyl dianhydrides. Work is currently underway to investigate this hypothesis.

Despite the undesirable aspect of low  $T_g$ 's, all of the PBDE resins exhibited the desirable aspect of processing easier than PMR-15 and AMB-21. While compression molding the powders, a large amount of flashing developed for the PBDE formulations. In order for the resin to remain in the mold and furnish an acceptable disk, the powders had to be B-staged for an additional 0.5 hrs. at 288°C. Meanwhile, the PMR-15 and AMB-21 molding powders did not require this additional B-staging. It is evident that the PBDE resins have lower melt viscosities than the controls, but exact measurements of the melt viscosities has yet to be made.

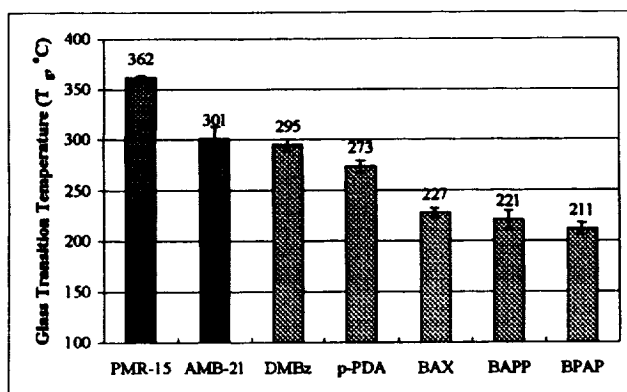


Figure 3. Average  $T_g$  values of the postcured resin discs measured by TMA ( $10^\circ\text{C}/\text{min.}$ ). PMR-15 and AMB-21 are the controls. Each diamine (DMBz, *p*-PDA, BAX, BAPP, and BPAP) has been substituted into the PBDE/DIAMINE/NE,  $n=2$  scheme.

An isothermal weight loss study was performed at  $288^\circ\text{C}$  for 1000 hrs., and the results are shown in Figure 4. All of the PBDE resins show a lower weight loss than AMB-21 (6.8%), and the DMBz (5.6%) and *p*-PDA (5.4%) disks show a weight loss comparable to PMR-15 (4.8%). Generally, as the number of ether linkages increase, the weight loss also increases and the thermal-oxidative stability decreases. Ether linkages provide a source of flexibility, but unfortunately they are relatively thermally unstable and provide a degradation pathway. The only exception to the trend is seen in the BPAP formulation (5.9%), but after 2000 hrs. at  $288^\circ\text{C}$ , it was observed that the weight loss increases past the AMB-21 resin and compares to the BAX formulation.

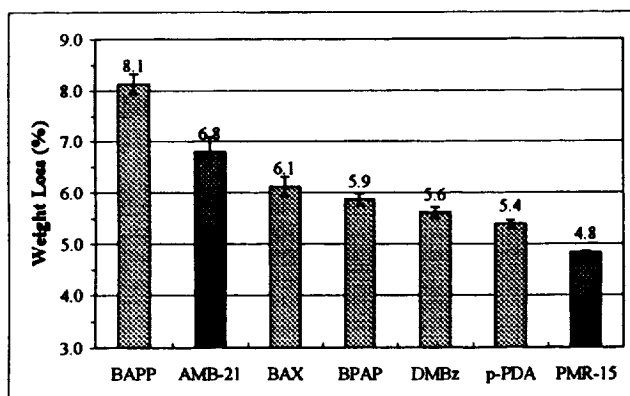


Figure 4. Average weight loss percentages at  $288^\circ\text{C}$  for 1000 hrs. PMR-15 and AMB-21 are the controls, and the diamines were substituted into the PBDE/DIAMINE/NE,  $n=2$  scheme.

**Molecular Weight Variation.** The dependence of molecular weight ( $n$  value) on  $T_g$  and TOS was investigated with the best performing resin, PBDE/DMBz/NE. Table 1 displays two trends: as the molecular weight between crosslinks increases, the  $T_g$  decreases and the TOS increases. As expected, the polymer stiffens as the molecular weight between crosslinks decreases (i.e. increase  $T_g$ ), but at the same time the concentration of aliphatic nadic ester endcap increases (i.e. increase weight loss).

Table 1. Molecular Weight Dependence on  $T_g$  and TOS

PBDE/DMBz/NE	Weight Loss (%)	
$n$ value	$T_g$ ( $^\circ\text{C}$ )	[1000 hrs., $288^\circ\text{C}$ ]
3	257	5.0
2	292	5.6
1	331	7.5

**Final Postcure Temperature Variation.** In an attempt to advance the  $T_g$ 's of the PBDE containing neat resins, the final postcure temperature was varied from  $316^\circ\text{C}$  to  $357^\circ\text{C}$ . The temperature ramps were identical, and the samples held at the final postcure temperature for 12 hrs. All PBDE resins displayed a maximum  $T_g$  value at the final postcure temperature of  $329^\circ\text{C}$ . The only exception was the PBDE/DMBz/NE,  $n=1$  formulation which showed a maximum  $T_g$  of  $351^\circ\text{C}$  at  $316^\circ\text{C}$  postcure. This  $T_g$  value is approaching that of PMR-15, but the thermal stability of the  $n=1$  resins may be poor. The  $T_g$  values of the postcured DMBz resins ( $n=1,2,3$ ) are shown in Figure 5. It can be seen that the  $n=1$  curve drastically slopes downward with increasing postcure temperature, presumably due to a higher degree of degradation at higher postcure temperatures.

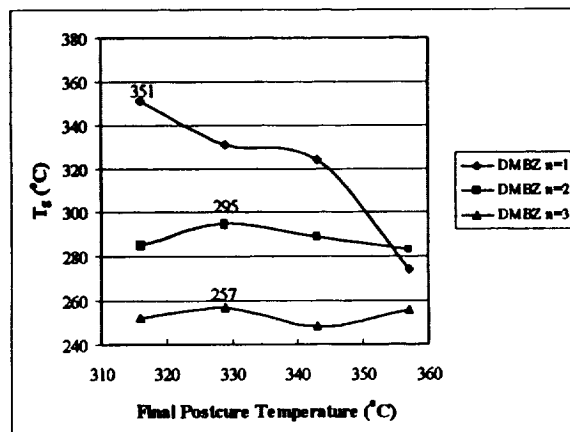


Figure 5. The effect of final postcure temperature on the  $T_g$  of PBDE neat resins (measured by TMA,  $10^\circ\text{C}/\text{min.}$ ). DMBz is the diamine, and the calculated molecular weight was varied from  $n=1$  to  $n=3$ .

## Conclusions

The use of non-coplanar monomers in PMR polyimides can increase melt flow and processability. The glass transition temperatures are not high enough for many high temperature applications, but weight loss values for the  $n=2$  resin appear favorable. Ongoing work to improve  $T_g$ , lower weight loss, and quantitatively measure melt viscosity is underway.

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